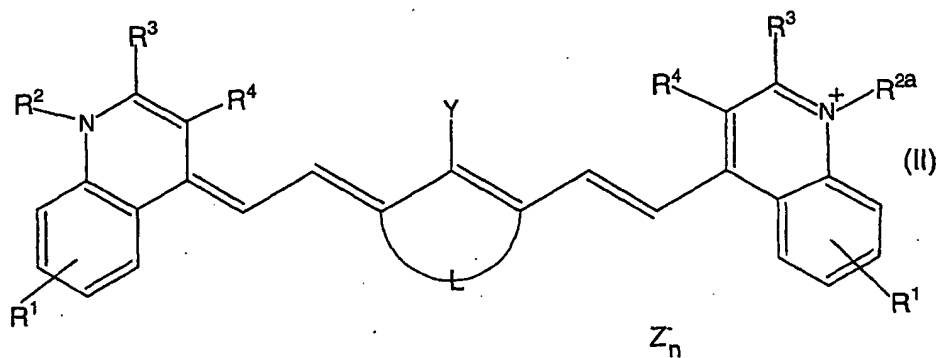
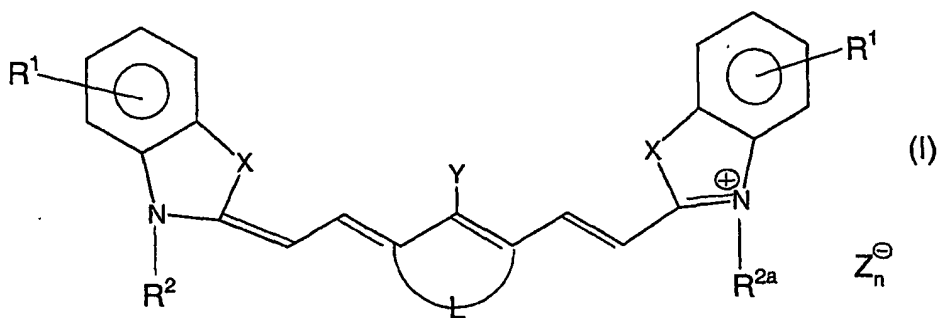


# Claims

1. Process for the production of a meso-substituted cyanine dye of the formula (I) or (II)



wherein

each  $R^1$  is independently selected from  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ , a hydrogen atom, an optionally substituted  $\text{C}_1\text{-C}_{12}$  alkyl, halogen, optionally substituted  $\text{C}_1\text{-C}_{12}$  alkoxy,  $-\text{NO}_2$ ,  $-\text{CN}$  and fused aromatic and heteroaromatic ring systems,

each  $X$  independently represents  $-\text{CR}^3=\text{CR}^4-$ ,  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{NR}^6-$  or  $-\text{CR}^5_2-$ ,

$R^2$  is an optionally substituted  $\text{C}_1\text{-C}_{12}$  alkyl, an optionally substituted aryl,  $-(\text{C}_1\text{-C}_{12} \text{ alkanediyl})-\text{SO}_3\text{H}$  or  $-(\text{C}_1\text{-C}_{12} \text{ alkanediyl})-\text{COOH}$ ,

$R^{2a}$  is an optionally substituted  $\text{C}_1\text{-C}_{12}$  alkyl, an optionally substituted aryl,  $-(\text{C}_1\text{-C}_{12} \text{ alkanediyl})-\text{SO}_3^-$ ,  $-(\text{C}_1\text{-C}_{12} \text{ alkanediyl})-\text{COO}^-$  or  $-(\text{C}_1\text{-C}_{12} \text{ alkanediyl})-\text{NR}^6_3^+$ ,

$R^3$  and  $R^4$  are independently selected from  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COOR}^6$ ,  $-\text{CN}$ ,  $-\text{NO}_2$ ,  $-\text{OH}$ ,  $-\text{NR}^6_2$ , a hydrogen atom, an optionally substituted  $\text{C}_1\text{-C}_{12}$  alkyl, an optionally substituted  $\text{C}_1\text{-C}_{12}$  alkoxy, halogen and aryl,

each  $R^5$  is independently  $\text{C}_1\text{-C}_{12}$  alkyl,

$Z^-$  is selected from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{aryl-SO}_3^-$ ,  $\text{alkyl-O-SO}_3^-$ ,  $\text{PO}_4\text{H}_2^-$ ,  $\text{CH}_3\text{SO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$  and  $\text{ClO}_4^-$ ,

$n$  is 0 if  $R^{2a}$  is  $-(\text{C}_1\text{-C}_{12} \text{ alkanediyl})-\text{SO}_3^-$  or  $-(\text{C}_1\text{-C}_1 \text{ alkanediyl})-\text{COO}^-$ ,

$n$  is 1 if  $R^{2a}$  is an optionally substituted  $\text{C}_1\text{-C}_{12}$  alkyl or aryl,

$n$  is 2 if  $R^{2a}$  is  $-(\text{C}_1\text{-C}_{12} \text{ alkanediyl})-\text{NR}^6_3^+$ ,

$Y$  is selected from  $-\text{S-Ar}$ ,  $-\text{Se-Ar}$ ,  $-\text{O-Ar}$ ,  $-\text{NR}^6\text{-Ar}$ ,  $-\text{SO}_2\text{-Ar}$  and  $-(\text{N-heterocycle})$ ,

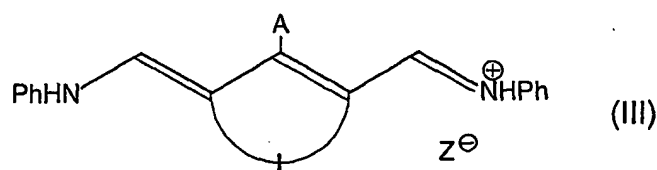
$R^6$  is a hydrogen atom or an optionally substituted  $\text{C}_1\text{-C}_{12}$  alkyl,

$\text{Ar}$  is an aromatic group wherein one or more ring carbon atoms are optionally replaced with heteroatoms selected from N, O and S, and



represents  $\text{C}_2\text{-C}_3$  alkanediyl, optionally comprising one or more substituents selected from  $\text{C}_1\text{-C}_{10}$  alkyl,  $\text{C}_1\text{-C}_{10}$  alkoxy, aryl and halogen atoms,

said process comprising the single-step reaction of the dye of formula (III)



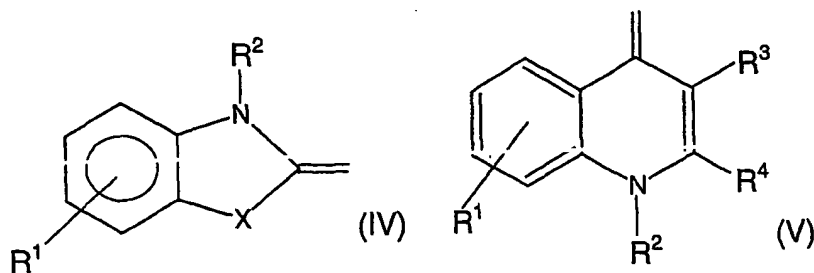
wherein A is selected from Cl and Br and



is as defined above for formulas (I) and (II), with

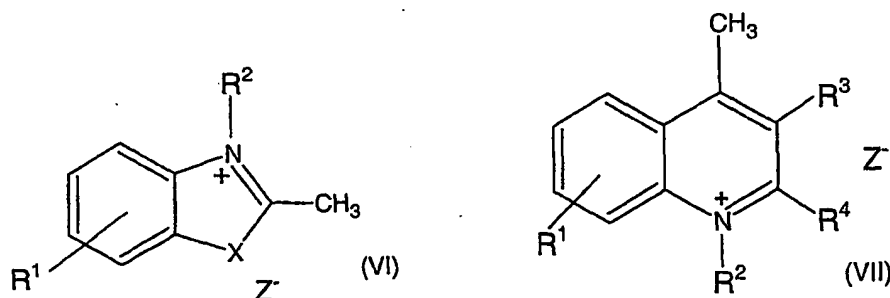
(a) a compound selected from

(i) a methylene derivative of formula (IV) or (V)



and


(ii) a quaternary salt of formula (VI) or (VII),




wherein X, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and Z are as defined in formulas (I) and (II), and

(b) a compound selected from

(i) aromatic and heteroaromatic functionalized compounds Ar-B,

(ii) saturated 5- or 6-membered cyclic amines  and


(iii) 5- or 6-membered heteroaromatic compounds  comprising at least one nitrogen atom as heteroatom in the aromatic ring, which nitrogen atom is bonded to the two adjacent ring carbon atoms via a single and a double bond and furthermore comprises a free electron pair


wherein

Ar represents a 5- or 6-membered aryl, wherein one or more ring carbon atoms are optionally replaced with heteroatoms selected from N, O and S,

B is selected from -NHR<sup>6</sup>, -SH, -OH, -SeH and -SO<sub>2</sub>H,

$R^6$  is a hydrogen atom or an optionally substituted  $C_1$ - $C_{12}$  alkyl and the saturated cyclic amines optionally comprise an additional heteroatom selected from N, O and S in the ring, in an inert organic solvent miscible with water.

2. Process according to claim 1, wherein the dye (III) is reacted with at least one methylene compound (IV) or at least one quaternary salt (VI) and a compound (b), and a cyanine dye of formula (I) is obtained.
3. Process according to claim 1, wherein the dye (III) is reacted with at least one methylene compound (V) or at least one quaternary salt (VII) and a compound (b), and a cyanine dye of formula (II) is obtained.
4. Process according to any of claims 1 to 3, wherein  represents  $-CH_2-CH_2-$  or  $-CH_2-CH_2-CH_2-$ .
5. Process according to any of claims 1 to 4, wherein Y represents  $-S-Ar$ .
6. Process according to any of claims 1 to 5, wherein only one methylene derivative or quaternary salt is used and a dye with a symmetrical structure I or II is obtained.
7. Process according to any of claims 1 to 6, wherein the compound (b) and the dye (III) are provided in the reaction vessel and the methylene compound or the quaternary salt is added in dissolved form.
8. Process according to any of claims 1 to 7, wherein an alkali hydroxide is added to the reaction mixture if B is selected from  $-SH$ ,  $-OH$ ,  $-SeH$  and  $-SO_2H$ .
9. Process according to any of claims 1 to 8, wherein a quaternary salt (VI) or (VII) is used and an amount of a base equimolar to the amount of quaternary salt is added to the reaction mixture.

10. Process according to any of claims 1 to 9, wherein the cyanine dye (I) or (II) is precipitated by the addition of a mineral acid.
11. Process according to any of claims 1 to 10, wherein compound (b) is a (hetero)aromatic functionalized compound Ar-B.
12. Process according to any of claims 1 to 4 and 6 to 10, wherein compound (b) is a heteroaromatic compound .
13. Process according to any of claims 1 to 12, wherein the obtained cyanine dye (I) or (II) is subsequently subjected to an extraction with a non-solvent.
14. Process according to any of claims 1 to 13, wherein the obtained cyanine dye (I) or (II) is subjected to an anion exchange.